A Comparative Study on the Corrosion Performance of Ni₄₇Ti₄₉Co₄ and Ni₅₁Ti₄₉ Shape Memory Alloys in Simulated Saliva Solution for Dental Applications

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Abstract In this study, the corrosion behavior of Ni₄₇Ti₄₉Co₄ shape memory alloy (SMA) was investigated in simulated saliva solution with the binary alloy Ni₅₁Ti₄₉ as a reference. The surface morphology and the chemical composition of the oxide films were characterized by scanning electron microscopy and X-ray photoelectron spectroscopy before and after immersion in the test solutions, respectively. The results showed that the ternary alloy was less affected by the test solution, owing to the formation of passive layer composed mainly of the oxides of titanium and cobalt in several oxidation states. Cyclic voltammetry, electrochemical impedance spectroscopy and potentiodynamic polarization measurements affirmed that the passive oxide film significantly improved the corrosion resistance of Ni₄₇Ti₄₉Co₄ SMAs as demonstrated by the smaller corrosion current density, larger resistance and smaller capacitance. Consequently, alloying with cobalt, which has paramount importance in enhancing the passive layer, expands the use of Ni₄₇Ti₄₉Co₄ SMAs in dental work as new nitinol alloys with high corrosion resistances.

KEY WORDS: Ni₄₇Ti₄₉Co₄; Shape memory alloy (SMA); Corrosion; Artificial saliva; X-ray photoelectron spectroscopy (XPS)

1 Introduction

Biomedical implants are becoming increasingly important for patients to decrease pain and improve their quality of life through surgical procedures. Contrary to traditional metallic biomaterials, NiTi alloys as intermetallic materials have been attracting a great interest in various applications as electronics, robotics [1], as well as a platform material in

cardiovascular [2], dental [3] and orthopedic biomedical devices [4–6].

These implants combine the advantages of high superior pseudoelasticity, unique shape memory effect and good mechanical properties. It is well established that a stable oxide film on NiTi SMA surface is composed mainly of titanium-rich oxide, which helps to resist corrosion in physiological fluids [7]. Although NiTi alloy has favorable biocompatibility with human body fluids [8–11], the principal drawback of these alloys in biomedical applications is the release of nickel ions during corrosion process, leading to an allergic, toxic and even carcinogenic reaction into the surrounding tissue [12, 13]. Consequently, it is crucial to improve the corrosion resistance of NiTi alloys for their potential biomedical applications. To achieve this, extensive investigation has been carried out on the surface treatment and composition design [14–16]. One of the most effective approaches to the composition design is alloying additional elements for better corrosion resistance

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performance and novel mechanical properties. It was reported that incorporation of one or more elements into the binary alloy altered the alloy composition and affected the phase transition. Therefore, changing the chemical composition of the alloy, which plays an important role in the alloy passive layer, is an ideal step for enhancing corrosion resistance and optimizing the surface properties [17].

For successful implantation, the corrosion resistance of a new type of biomedical material has to be studied in physiological environment which significantly affects the experimental results of corrosion behavior and biocompatibility. In the oral cavity, saliva, secreted by salivary glands, acts as the most basic corrosion environment for dental materials. It is composed of mainly salt solutions with a variety of mucus, glycoproteins, lipids, enzymes and antibacterial compounds [18]. Obviously, facing a corrosive oral environment for long time would induce damage to the oxide film covering the alloy surface [19, 20], allowing active metal to be released and inducing toxic reactions between the host tissue and the foreign implants [21–24]. In continuation to our work [25], the corrosion resistance of the newly ternary alloy $\text{Ni}_{47}\text{Ti}_{49}\text{Co}_4$ SMAs has been studied in physiological body fluid to confirm its biocompatibility. The present study intends to investigate surface microstructure and oxide film characterization of $\text{Ni}_{51}\text{Ti}_{49}$ and $\text{Ni}_{47}\text{Ti}_{49}\text{Co}_4$ SMAs in simulated saliva solution by scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). The dissolved corrosion products will be determined by inductively coupled plasma (ICP). Further investigation will be conducted on the effect of cobalt addition on enhancing the corrosion resistance of $\text{Ni}_{51}\text{Ti}_{49}$ in the same solution, making it a promising step toward its use for dental applications.

2 Experimental

2.1 Products and Reagents

All solvents and chemicals were in reagent purity grade and used as received. Artificial saliva was used as the electrochemical test electrolyte which consisted of NaCl (400 mg/L), KCl (400 mg/L), $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (795 mg/L), $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ (690 mg/L), KSCN (300 mg/L), $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ (5 mg/L) and urea (1000 mg/L); temperature of $37 \pm 1^\circ\text{C}$; pH ≈ 6.8 [26].

2.2 Alloys Preparation

$\text{Ni}_{51}\text{Ti}_{49}$ and $\text{Ni}_{47}\text{Ti}_{49}\text{Co}_4$ SMAs (fabricated by melting technique under vacuum) were used as test materials. The atomic percent of $\text{Ni}_{51}\text{Ti}_{49}$ is 51% Ni and 49% Ti, while

that of $\text{Ni}_{47}\text{Ti}_{49}\text{Co}_4$ is 47% Ni, 49% Ti and 4% cobalt. Cubic-shaped specimens of 0.5 cm^3 were cut from the original alloys. An electric wire was welded to each alloy for connection. Then the alloys were covered with epoxy resin leaving an exposed surface area of 0.2 cm^2 . Prior to each experiment, the specimens were mechanically polished with a series of abrasive papers of 400, 800, 1500 grades and cleaned ultrasonically with ethanol for 15 min at ambient temperature and then washed with distilled water. Prior to electrochemical corrosion testing, the specimens were submerged into deaerated electrolyte without any imposed potential for 30 min.

2.3 Materials Characterization

A scanning electron microscope (Jeol Jxa-840A) was used for the visualization and the evaluation of the morphological, structural and chemical features of the alloy surfaces. SEM images were taken pre- and post-immersion of both alloys in artificial saliva for 14 days. Perkin-Elmer Optima 2100 Dual View inductively coupled plasma optical emission spectrometry (ICP-OES) instrument connected with AS 93 Plus auto-sampler was used for elemental analysis. Surface chemical composition of both alloys before and after immersion in artificial saliva was achieved by X-ray photoelectron spectroscopy (XPS). Measurements were carried out using a monochromatic $\text{AlK}\alpha$ X-ray source operating at 150 W (Kratos Axis Ultra DLD). The survey and high-resolution spectra were collected at fixed analyzer pass energies of 160 and 20 eV, respectively. Detection limits were approximately 0.05–1.0 at.%. Major factors affecting detection limits were the element itself (heavier elements generally having lower detection limits), interferences (including photoelectron peaks and Auger electron peaks from other elements) and background (mainly caused by signal from electrons that have lost energy to the matrix). Both alloys were polished and degreased in ethyl alcohol in an ultrasound washer for 15 min, and then immersed in the artificial saliva for 6 h and then rinsed, dried by acetone and transferred into a vacuum system. The XPS measurements were always performed at least four areas on the surface.

2.4 Electrochemical Characterization

The corrosion behavior was evaluated in artificial saliva by cyclic voltammetry (CV), electrochemical impedance spectrum (EIS) and potentiodynamic polarization measurements using a potentiostat/galvanostat (Model 73022, Autolab Instruments, Metrohm) with NOVA software. All measurements were carried out in conventional three-electrode cell configuration with platinum, $\text{Ag}/\text{AgCl}/3\text{ mol/L KCl}$ (Satd.) and the alloy, as counter, reference

and working electrode, respectively. Cyclic voltammetric tests were started at a potential -1.0 V by scanning at 10 mV s^{-1} toward more positive potentials up to 1.5 V (vs. Ag/AgCl), and then, the scanning was reversed toward the initial potential. The electrochemical experiments were performed by applying a sinusoidal potential perturbation of 10 mV at the open-circuit potentials. The impedance spectra were measured with frequency domain from 100 kHz down to 100 mHz . The real (Z) and imaginary (Z') parts of the impedance are calculated from the overall impedance (Z^*) as in Eq. (1):

$$Z^*(\omega) = Z(\omega) + jZ'(\omega) \quad (1)$$

where ω is the angular frequency that equals to $2\pi f$ (f /Hz is the frequency). The EIS was plotted in the form of complex plane diagrams (Nyquist and Bode plots).

The potentiodynamic curves were studied for $\text{Ni}_{51}\text{Ti}_{49}$ and $\text{Ni}_{47}\text{Ti}_{49}\text{Co}_4$ SMAs with a scan rate of 1 mV s^{-1} . The corrosion currents were determined by the intersection of the cathodic or the anodic Tafel line with the open-circuit potential (OCP, potential of zero current in the potentiodynamic curves or E_{corr}). This point determines the potential (E_{corr}) and current density (i_{corr}) for corrosion. By using a computer least squares analysis, the Tafel constants were calculated as the slope of the points after E_{corr} . For all tested alloys, the active dissolution parameter values, corrosion potential (E_{corr}), corrosion current density (i_{corr}) and Tafel slopes (β_a and $-\beta_c$) are calculated and presented in Table 2. The same samples were used in the impedance and potentiodynamic polarization studies. Each measurement was repeated twice to improve the statistics and confirm reproducibility.

3 Results and Discussion

3.1 Surfaces Morphologies and Film Characterization

3.1.1 Surface Morphology

It is well known that the corrosion behavior is significantly influenced by the microstructure and phase distribution. SEM was used to observe the microstructure of $\text{Ni}_{51}\text{Ti}_{49}$ and $\text{Ni}_{47}\text{Ti}_{49}\text{Co}_4$ SMAs surface before and after immersion in artificial saliva solutions for 14 days at 37 ± 1 °C. Images before immersion in artificial saliva are shown in Fig. 1a, b, indicating smooth, uniform and free pore surface for $\text{Ni}_{51}\text{Ti}_{49}$ and $\text{Ni}_{47}\text{Ti}_{49}\text{Co}_4$ SMAs, whereas some scratches were also observed on both surfaces due to polishing. However, after immersion in saliva, the surface of $\text{Ni}_{51}\text{Ti}_{49}$ SMA was roughened with corrosion pits (Fig. 1c, e), while the pits were small and shallow on $\text{Ni}_{47}\text{Ti}_{49}\text{Co}_4$

SMA (Fig. 1d, f). These observations indicated that $\text{Ni}_{47}\text{Ti}_{49}\text{Co}_4$ SMA was not greatly affected by the artificial saliva. The difference in the behavior between the two alloys may be associated with their difference in composition, which is altered by cobalt addition and had influenced the corrosion behavior of $\text{Ni}_{51}\text{Ti}_{49}$ SMA [27, 28]. Consequently, decreasing Ni content in the alloy retards dissolution and pitting corrosion.

3.1.2 Ion Release

Metallic ion release from $\text{Ni}_{47}\text{Ti}_{49}\text{Co}_4$ and $\text{Ni}_{51}\text{Ti}_{49}$ SMA was analyzed in artificial saliva solution via ICP. Results from immersion tests revealed that, for both alloys, Ti ion release was significantly lower than Ni. However, no cobalt ion release was detected. $\text{Ni}_{51}\text{Ti}_{49}$ SMA exhibited distinct corrosion activity and a high quantity of Ni ions was released by 0.532 mg/L , while $\text{Ni}_{47}\text{Ti}_{49}\text{Co}_4$ SMA presented a low value of Ni ion release by 0.010 mg/L [27, 28]. Consequently, the detected amount of Ni ion released from $\text{Ni}_{47}\text{Ti}_{49}\text{Co}_4$ was less than the critical amount that would lead to allergic reactions in the body, which has been specified as $0.12\text{--}0.5 \text{ mg/L}$ [29]. Therefore, the $\text{Ni}_{47}\text{Ti}_{49}\text{Co}_4$ SMA used in this study was medically acceptable for dental applications based on the amount of Ni ions released in the artificial saliva solution.

3.1.3 X-Ray Photoelectron Spectroscopy (XPS)

The elemental composition of the passive layer formed on the surface of $\text{Ni}_{47}\text{Ti}_{49}\text{Co}_4$ and $\text{Ni}_{51}\text{Ti}_{49}$ SMA before and after immersion in artificial saliva was studied by XPS as shown in Fig. 2. It should be noted that SMAs gain their shape memory effects from their thermoelastic martensitic transformation. However, transition, mechanical, thermal properties and microstructure of SMAs are affected greatly by the ion types [17]. As a result the chemical composition of the alloy significantly affects the oxide film structure that formed on the surfaces during immersion experiments. Figure 2a, b reveals that the main compositions of the surface layer for $\text{Ni}_{51}\text{Ti}_{49}$ and $\text{Ni}_{47}\text{Ti}_{49}\text{Co}_4$ before immersion in artificial saliva solution are carbon (C 1s), titanium (Ti 2p_{3/2}), nickel (Ni 2p_{3/2}) and oxygen (O 1s), while cobalt (Co 2p) is only observed in Fig. 2b. The high-resolution carbon (C 1s) spectrum was originated from so-called environmental contamination. In Fig. 2c, d, after immersion in artificial saliva, chloride (Cl 2p_{3/2}), sulfur (S 2p_{3/2}), calcium (Ca 2p_{3/2}) and phosphorous (P 2p_{3/2}) peaks were observed with binding energy 198, 166, 348 and 190 eV, respectively, and all these were retrieved from the saliva solution. It is also assumed that the high-resolution spectrum at 530.7 eV denoted as O 1s is assigned to oxygen atoms (O^{2-}) in the form of oxides. Thus, the composition

Fig. 1 SEM micrographs of surface morphology: $\text{Ni}_{51}\text{Ti}_{49}$ **a** and $\text{Ni}_{47}\text{Ti}_{49}\text{Co}_4$ **b** SMAs before immersion in artificial saliva solution; $\text{Ni}_{51}\text{Ti}_{49}$ **c**, **e** and $\text{Ni}_{47}\text{Ti}_{49}\text{Co}_4$ **d**, **f** SMAs after immersion in artificial saliva solution for 14 days with different magnifications

of the outermost surface layer of both samples is mainly TiO_2 . Figure 2c depicts the XPS survey spectrum of $\text{Ni}_{51}\text{Ti}_{49}$ SMA after immersion, where high contents of TiO_2 , Ti_2O_3 and metallic titanium with binding energy 458.62, 464.84 and 454.94 eV, respectively, were found in the oxide layer. Simultaneously, different intermediate phases from Ni and Ti oxides were formed beneath the oxide layer, where Ni may diffuse into the sublayer and to the outermost layer forming unstable oxides on $\text{Ni}_{51}\text{Ti}_{49}$ SMA surface, and these oxides were observed at 855.7 and 869.5 eV. Consequently, Ni ions could be easily released and thus entered into the electrolyte [25].

The XPS survey spectrum of the $\text{Ni}_{47}\text{Ti}_{49}\text{Co}_4$ SMA illustrated in Fig. 2d exhibits quite different behaviors after immersion in artificial saliva solution, in which the intensity of Ni peaks decreases due to the low Ni content found in the sublayers. Thus, the outermost layer is formed mainly from stable TiO_2 [30]. In addition, Co oxides appeared in the outermost layer at 776.4 and 796.6 eV forming mixed oxides on $\text{Ni}_{47}\text{Ti}_{49}\text{Co}_4$ surface [31]. Finally, minimizing Ni content by addition of 4 at.% cobalt into the binary alloy changes the chemical composition and the grain size of the alloy. This replacement altered the microstructure and phase transition affecting the chemical and mechanical behavior of the ternary alloy. Moreover, addition of 4 at.% cobalt leads to improvement in the film passivity which plays an important role in alloy protection, resulting in significant enhancement in the corrosion resistance of the $\text{Ni}_{47}\text{Ti}_{49}\text{Co}_4$ SMAs.

3.2 Cyclic Voltammetry Analyses

Figure 3 shows the comparison between the cyclic voltammetric curves of $\text{Ni}_{51}\text{Ti}_{49}$ and $\text{Ni}_{47}\text{Ti}_{49}\text{Co}_4$ SMAs in artificial saliva solution at 37 ± 1 °C with scanning rate of 10 mV s^{-1} . The cyclic voltammetric curve of $\text{Ni}_{51}\text{Ti}_{49}$ suggests the formation and growth of the oxide film on the alloy's surface during anodic reaction [25]. The anodic current increased sharply with an anodic peak at about +0.81 V, indicating localized anodic dissolution, and starting of pitting corrosion. In the backward scan, the cathodic current rapidly decreased forming a cathodic peak at about −0.83 V, suggesting the dissolution of the oxide film. In contrary, the cyclic voltammetric curve for $\text{Ni}_{47}\text{Ti}_{49}\text{Co}_4$ SMA exhibited low anodic and cathodic currents, suggesting the formation of passive film on the ternary alloy. Therefore, different behaviors in the anodic and cathodic current for both alloys are basically due to the presence of cobalt, which gives rise to different characteristics of the oxide film formed on $\text{Ni}_{47}\text{Ti}_{49}\text{Co}_4$ SMAs surface during the anodic and cathodic scan. The cyclic voltammetric results come in good agreement with XPS results.

3.3 EIS Measurements

Electrochemical impedance measurements were performed for exploring the properties and the passivity of $\text{Ni}_{51}\text{Ti}_{49}$ and $\text{Ni}_{47}\text{Ti}_{49}\text{Co}_4$ SMAs surfaces. EIS can lead to full

Fig. 2 XPS survey spectra: $\text{Ni}_{51}\text{Ti}_{49}$ **a** and $\text{Ni}_{47}\text{Ti}_{49}\text{Co}_4$ **b** SMAs before immersion in artificial saliva solution; $\text{Ni}_{51}\text{Ti}_{49}$ **c** and $\text{Ni}_{47}\text{Ti}_{49}\text{Co}_4$ **d** SMAs after immersion in artificial saliva solution

Fig. 3 Cyclic voltammograms: $\text{Ni}_{51}\text{Ti}_{49}$ **a** and $\text{Ni}_{47}\text{Ti}_{49}\text{Co}_4$ **b** SMAs in artificial saliva at $37 \pm 1^\circ\text{C}$ and scan rate of 10 mV s^{-1}

understanding of the processes that take place on $\text{Ni}_{51}\text{Ti}_{49}$ and $\text{Ni}_{47}\text{Ti}_{49}\text{Co}_4$ SMAs surface and the effect of cobalt on enhancing surface oxide film [25, 28]. As discussed previously, immersion experiment could produce strongly bonded film on the alloy surface, and the properties of this oxide film are altered by the alloy composition. Thus, variation in the electrochemical results would be noticed, suggesting corrosion resistance efficiency.

3.3.1 Bode and Nyquist Plots

Figure 4a–d depicts impedance spectra of $\text{Ni}_{51}\text{Ti}_{49}$ and $\text{Ni}_{47}\text{Ti}_{49}\text{Co}_4$ SMAs in a form of Nyquist and Bode plots at E_{corr} after immersion in saliva at $37 \pm 1^\circ\text{C}$. At earlier immersion hours, the magnitude of the impedance of both plots of $\text{Ni}_{51}\text{Ti}_{49}$ and $\text{Ni}_{47}\text{Ti}_{49}\text{Co}_4$ SMAs decreases slightly with increasing polarization time, suggesting the formation

Fig. 4 Experimental data in artificial saliva solution with immersion time till 15 h at 37 ± 1 °C: Nyquist plots **a, b**; Bode plot **c, d** for $\text{Ni}_{51}\text{Ti}_{49}$ and $\text{Ni}_{47}\text{Ti}_{49}\text{Co}_4$ SMAs, respectively

of porous oxide films on the surfaces of the alloys, and starting ions deposition from the saliva solution over the alloys [30].

Figure 5a, c demonstrates the EIS data as a complex impedance diagram (Nyquist plot), where the imaginary component $-Z$ of the impedance was plotted as a function of the real component Z for $\text{Ni}_{51}\text{Ti}_{49}$ (a) and $\text{Ni}_{47}\text{Ti}_{49}\text{Co}_4$ (b) SMAs at different immersion time till 72 h. $\text{Ni}_{47}\text{Ti}_{49}\text{Co}_4$ SMA shows higher resistance and lower capacitance than the $\text{Ni}_{51}\text{Ti}_{49}$ SMA (Table 1), and it is reflected by the Nyquist plots (Fig. 5a, c) in which the diameter of the capacitive loop of $\text{Ni}_{47}\text{Ti}_{49}\text{Co}_4$ SMA is large. In general, the materials that exhibited lower capacitance and higher resistance offer better corrosion resistance and vice versa [32]. Moreover, Fig. 5b and d shows the Bode plots of $\text{Ni}_{51}\text{Ti}_{49}$ (a) and $\text{Ni}_{47}\text{Ti}_{49}\text{Co}_4$ (b) SMAs at various immersion time till 168 h. For $\text{Ni}_{47}\text{Ti}_{49}\text{Co}_4$ SMA, $\log|Z|$ is linear with $\log f$, which is symptomatic of a predominantly capacitive behavior at the electrode/solution interface. In the frequency range of 10^2 – 10^{-2} Hz, θ has a value close to 70° which increases with time till 168 h. However,

$\text{Ni}_{51}\text{Ti}_{49}$ SMA showed lower capacitive behavior with θ value close to 60° . It is clear that the difference in the phase angle values reflects structural changes inside the surface layer (Fig. 5b, d), which is also comes in a good agreement with the XPS results. Additionally, it can also be clearly observed that bode magnitude presented in the high-frequency region went down for $\text{Ni}_{51}\text{Ti}_{49}$ SMA. These findings suggested that $\text{Ni}_{47}\text{Ti}_{49}\text{Co}_4$ SMA has high passivity film [33, 34], which offers an excellent protection to the alloy surface from aggressive ions in saliva solution as well as reduces the Ni ion release providing high corrosion resistance in the simulated oral environment rather than the binary alloy. Consequentially, $\text{Ni}_{47}\text{Ti}_{49}\text{Co}_4$ SMA would be a good candidate for the oral implants.

3.3.2 AC Impedance Analyses

EIS data were fitted to the proposed electrical equivalent circuits shown in Fig. 6 for $\text{Ni}_{51}\text{Ti}_{49}$ and $\text{Ni}_{47}\text{Ti}_{49}\text{Co}_4$ SMAs in artificial saliva solution at 37 ± 1 °C. EIS data of $\text{Ni}_{51}\text{Ti}_{49}$ SMA were fitted by a two-time constant

Fig. 5 Experimental data in artificial saliva solution with immersion time till 168 h at 37 ± 1 °C: Nyquist plots **a, c** and Bode plot **b, d** of $\text{Ni}_{51}\text{Ti}_{49}$ **a** and $\text{Ni}_{47}\text{Ti}_{49}\text{Co}_4$ **b** SMAs, respectively

equivalent electrical circuit (Fig. 6a); similarly, this circuit is the same model that was found to be appropriate in previous corrosion studies [25]. The physical meaning for the proposed circuit is association with the inner layer formed on oxide metal interface (R_1 , CPE_1) and with the outer porous oxide layer formed on the surface (R_2 , CPE_2). R_1 and R_2 are the charge-transfer resistance at the oxide/electrolyte interface, and CPE_1 and CPE_2 are capacitors which replace the constant phase element, while R_s refers to solution resistance. The impedance of the CPE is defined as $Z_{\text{CPE}} = [Q(j\omega)n]^{-1}$, where the constant Q is a frequency-independent parameter of the CPE, $j\omega$ is a complex variable for sinusoidal perturbations with ω of $2\pi f$ [35]. Deviation of the exponent n from the ideal value n of 1 for pure capacitance indicates the presence of inhomogeneity due to surface roughness and/or adsorbed species [36].

EIS plot showed that the impedance spectra of $\text{Ni}_{47}\text{Ti}_{49}\text{Co}_4$ SMA appear with a higher straight line; therefore, the same equivalent circuit was used for fitting EIS data

including Warburg impedance in series with R_2 . This Warburg impedance indicates adsorption pseudocapacitance, where the corrosion mechanism is controlled not only by a charge-transfer process but also by a diffusion process [28]. The characteristics of the oxide film are reflected in the value of R_2 , which are significantly higher for $\text{Ni}_{47}\text{Ti}_{49}\text{Co}_4$ SMA, whereas the value of CPE_2 is slightly large for the passive oxide film, suggesting that some smoothing of the surface occurs. Good agreement between experimental data and simulated data is obtained, and the fitting results are shown in Table 1 for both alloys. Therefore, according to Table 1, the higher resistance and lower capacitance of $\text{Ni}_{47}\text{Ti}_{49}\text{Co}_4$ SMA reveal better corrosion resistance.

3.3.3 Potentiodynamic Polarization Measurements

Measurements of current–potential relation can offer more information on corrosion rates, passivity and pitting tendency. Therefore, potentiodynamic polarization experiments are

Table 1 Equivalent circuit analysis of impedance spectra in artificial saliva (data from Figs. 4, 5)

	t (H)	R_s (Ω cm ²)	R_1 (M Ω cm ²)	C_1 (Ω^{-1} cm ⁻² S ⁿ)	n_1	R_2 (k Ω cm ²)	C_2 (Ω^{-1} cm ⁻² S ⁿ)	n_2	W (k Ω cm ² S ^{-1/2})
Ni ₅₁ Ti ₄₉ SMA	5.00	25.0	3.3	1.3	0.83	53.1	3.3	0.91	–
	10.0	25.2	3.6	1.4	0.81	52.5	3.5	0.93	–
	15.0	25.4	3.8	1.5	0.83	51.4	3.6	0.91	–
	24.0	26.6	3.1	0.9	0.82	62.7	2.5	0.91	–
	72.0	26.8	2.8	0.8	0.81	64.2	2.7	0.91	–
	120	27.4	2.6	0.78	0.83	64.5	2.4	0.91	–
	144	28.2	2.4	0.65	0.82	64.8	2.45	0.91	–
	168	28.4	2.2	0.6	0.82	65.1	2.3	0.91	–
Ni ₄₇ Ti ₄₉ Co ₄ SMA	5.00	25.4	2.4	0.9	0.84	64.7	2.9	0.91	5.6
	10.0	25.6	2.6	1.2	0.83	63.2	2.7	0.91	5.4
	15.0	25.8	2.8	1.25	0.81	62.5	2.6	0.91	5.1
	24.0	27.8	1.7	0.7	0.84	68.5	1.9	0.91	6.4
	72.0	28.4	1.2	0.62	0.84	69.2	1.7	0.91	6.8
	120	28.6	0.8	0.55	0.81	69.8	1.5	0.91	7.2
	144	28.8	0.6	0.5	0.82	70.2	1.4	0.91	7.4
	168	30	0.2	0.4	0.83	70.4	1.2	0.91	7.6

t polarization time, R_s solution resistance, R_1 , R_2 resistance of the formed layers, C_1 , C_2 constant phase element capacitor, n_1 , n_2 inhomogeneity and surface defects, W Warburg impedance

Fig. 6 Proposed equivalent circuit: Ni₅₁Ti₄₉ **a** and Ni₄₇Ti₄₉Co₄ **b** SMAs used to obtain impedance parameters

performed on Ni₅₁Ti₄₉ and Ni₄₇Ti₄₉Co₄ SMAs after 1 h immersion in artificial saliva solution at 37 ± 1 °C and illustrated in Fig. 7. Polarization parameters including corrosion potential (E_{corr}), corrosion current density (i_{corr}), polarization resistance (R_p), anodic Tafel slope (β_a), cathodic Tafel slope ($-\beta_c$) and corrosion rate are obtained by using standard technique from the potentiodynamic polarization plots and listed in Table 2.

After immersion in saliva, as shown in Fig. 7, Ni₄₇Ti₄₉Co₄ SMA showed a shift of the polarization curve toward lower current density (i_{corr}) and more positive corrosion potential (E_{corr}), suggesting an improvement in the corrosion behavior [25]. Furthermore, R_p values

enhanced greatly compared to Ni₅₁Ti₄₉ SMA. The increase in the R_p value suggested the formation of a protective oxide film improving the corrosion resistance of the Ni₄₇Ti₄₉Co₄ in artificial saliva solution. In contrast, the significant decrease in R_p value for Ni₅₁Ti₄₉ SMA suggested the leaching of Ni ions, causing decrease in corrosion resistance. Obviously, the anodic region of the polarization curve describes dissolution of metals/elements, while the cathodic region describes the addition of released electrons from the anodic oxidation reaction. The representative polarization curve (Fig. 7b) showed that the cathodic branch of the polarization curve of Ni₄₇Ti₄₉Co₄ SMA shifted toward lower current density, suggesting that the

Fig. 7 Potentiodynamic polarization curves: Ni₅₁Ti₄₉ **a** and Ni₄₇Ti₄₉Co₄ **b** SMAs in artificial saliva solution at 37 ± 1 °C showing positive corrosion behavior for Ni₄₇Ti₄₉Co₄

Fig. 8 Current density versus time curves: Ni₅₁Ti₄₉ **a** and Ni₄₇Ti₄₉Co₄ **b** SMAs in artificial saliva solution at 37 ± 1 °C

Table 2 Electrochemical corrosion parameter values for Ni₅₁Ti₄₉ and Ni₄₇Ti₄₉Co₄ SMAs in artificial saliva solution at 37 ± 1 °C by Tafel plot analyses

Samples	E_{corr} (V vs. Ag/AgCl)	i_{corr} ($\mu\text{A cm}^{-2}$)	β_a (mV dec ⁻¹)	$-\beta_c$ (mV dec ⁻¹)	R_p (k Ω)	Corrosion rate (mm/year)
Ni ₅₁ Ti ₄₉	-0.46 ± 0.03	0.41 ± 0.05	23 ± 0.04	41 ± 0.06	43 ± 0.03	0.05 ± 0.01
Ni ₄₇ Ti ₄₉ Co ₄	-0.32 ± 0.04	0.15 ± 0.01	41 ± 0.02	38 ± 0.06	65 ± 0.02	0.01 ± 0.01

E_{corr} corrosion potential, i_{corr} corrosion current density, β_a rate of anodic half reaction, $-\beta_c$ rate of cathodic half reaction, R_p polarization resistance

cathodic reduction reactions were suppressed, while the anodic branch exhibited a typical passive anodic region higher than that of the binary alloy, suggesting that Ni₄₇Ti₄₉Co₄ SMA had better corrosion resistance than Ni₅₁Ti₄₉ SMA.

From Table 2, one can conclude that the corrosion process is controlled by anodic reaction, due to the increases in the anodic slope (β_a), while the cathodic slope ($-\beta_c$) appears to be not affected greatly, which is confirmed previously by the cyclic voltammetry. Furthermore, from the Tafel slopes (β_a and $-\beta_c$), corrosion rates were calculated to be 0.05 and 0.01 mm/year for Ni₅₁Ti₄₉ and Ni₄₇Ti₄₉Co₄ SMAs, respectively. Tafel results are consistent with previous reported values [37–39]. The potentiodynamic polarization and the EIS results confirmed that the passive film had an important effect on corrosion protection of Ni₄₇Ti₄₉Co₄ SMAs. These findings suggested that Ni₅₁Ti₄₉ SMA was more susceptible to corrosion in saliva solution owing to its microstructure [33].

3.3.4 Potentiostatic Measurements

The potentiostatic technique was used to study the film development on the alloys surface in the tested solution, and the current was measured as a function of applied

potential. Figure 8 displays the potentiostatic curves of Ni₅₁Ti₄₉ and Ni₄₇Ti₄₉Co₄ in simulated saliva solution at 37 ± 1 °C. According to the potentiodynamic results, -450 mV versus Ag/AgCl was applied. At this potential both Ni₅₁Ti₄₉ and Ni₄₇Ti₄₉Co₄ are under passive state. At the beginning, the current density dropped to a lower level, then stabilized after a few seconds. A low current density was observed for Ni₄₇Ti₄₉Co₄, with magnitude about 10⁻⁷ A/cm², while it was 10⁻⁶ A/cm² for Ni₅₁Ti₄₉. The high current density for Ni₅₁Ti₄₉ was attributed to the Ni ion release, which was confirmed previously by ICP [27]. The EIS studies and polarization tests results were in accordance with the SEM and XPS analysis.

4 Conclusion

In the current study, surface and elemental analysis as well as electrochemical and potentiodynamic measurements for Ni₄₇Ti₄₉Co₄ SMA was investigated in a comparative manner with Ni₅₁Ti₄₉ SMA via immersion experiments in artificial saliva solutions. The alloying of Ni₅₁Ti₄₉ SMA with cobalt altered the microstructure and phase transition of the binary alloy, and thus, improving its corrosion resistance. Furthermore, the formation of a passive layer

based on different types of oxides was enhanced with alloying cobalt, leading to more surface protection and less Ni ion release below the critical amount. Consequently, Ni₄₇Ti₄₉Co₄ SMA is believed to be suitable for the usage in dental applications with excellent corrosion resistance in oral media.

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